

# SURFACE CHEMICAL METHODS OF FORMING HARDPAN IN PYRRHOTITE TAILINGS AND PREVENTION OF THE ACID MINE DRAINAGE<sup>1</sup>

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**Abstract:** This work was undertaken to identify conditions under which hardpan could be formed in pyrrhotite (FeS) rich tailings using surface chemical methods and to check the susceptibility of the synthetic hardpan to atmospheric oxidation and acid formation.

Pyrrhotite hardpan was first grown on a small scale (200 g) by surface chemical and electrochemical methods, after treating the FeS-rich tailings with a dilute solution of Fe<sup>2+</sup>, pH adjustment, and curing for several weeks in the presence of air. This synthetic hardpan was similar to the pyrrhotite hardpans formed under natural conditions, consisting of FeS grains embedded in iron oxyhydrate (goethite) matrix.

Attempts were then made to grow similar hardpans on a large scale with FeS columns of 3 ft length and 4 in diameter. The effects of surface oxidation of FeS in air, Fe<sup>2+</sup> treatment, humidity, pH, and a water head (2 in) on the hardening of tailings and acid formation have been examined. Hardening was confined mainly to the outer layer of the tailings exposed to air; the inner core remained soft and retained most of the Fe<sup>2+</sup> in the unoxidized form. The pH, dissolved iron concentration, and redox potentials of the percolant solutions were monitored. Most pronounced was the effect of maintaining 2 in of water head on the tailings, which prevented the oxidation of FeS and acid formation completely. The data have been examined in light of the Eh-pH diagram of the FeS<sub>2</sub>-FeS-Fe<sub>2</sub>O<sub>3</sub> system in equilibrium with water. It is inferred that the FeS system can be stabilized through formation of iron oxide and other less soluble compounds such as iron silicates on the surfaces. Methods of improving kinetics of hardpan formation have been suggested.

**Additional Key Words:** acid mine drainage, pyrrhotite, hardpan, sulfides.

## Introduction

Natural formation of hardpans is often experienced in sulfide tailings that are exposed to air and water at the disposal sites. The hardpans normally consist of pyrrhotite (FeS) and pyrite (FeS<sub>2</sub>) grains cemented in iron oxyhydrate (goethite) structure. This phenomenon has been attributed to the Fe<sup>2+</sup> being oxidized to ferric oxyhydrates and forming hardpans in selective areas. Pyrite, being an electrocatalyst for oxygen reduction, undergoes little surface oxidation itself; hence pyrite hardpans are rare in nature.

In our earlier work (Ahmed and Giziewicz, 1992; Ahmed, 1990, 1991) in this field, the electrochemical and solid state properties of iron sulfides were examined, and the oxidative decomposition of iron sulfides was attributed to 'holes' or electron vacancies, formed as electrons are transferred from the substrate to oxygen or Fe<sup>3+</sup>. The holes are electrically mobile and lead to bond breaking and decomposition. It was also reported that FeS and FeS<sub>2</sub> can be electrochemically passivated by growing iron oxide films on the sulfide surfaces. The oxide film would then protect the sulfide substrate from further oxidation. The Eh-pH diagram of the FeS-FeS<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> system in equilibrium with water, as shown in fig. 1, indicates that iron sulfides under oxidizing conditions are unstable and produce acid and dissolved Fe<sup>2+</sup> and Fe<sup>3+</sup>. At sufficiently low pH, the dissolved Fe<sup>3+</sup> in turn causes further oxidation and decomposition of the sulfides. The sulfide oxidation by air can occur even in a basic medium. On the contrary, iron oxides, being the oxidation products, can form a stable phase under oxidizing conditions as long as the medium is neutral or basic. Also, iron oxides can be further stabilized by converting the surface into less soluble compounds.

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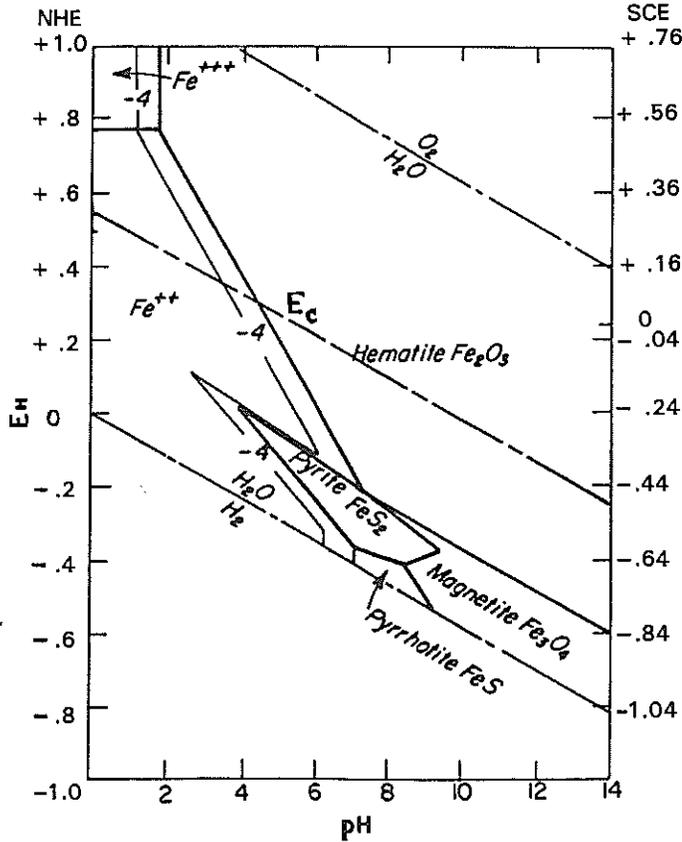


Figure 1. Eh-pH diagram showing the stability contours for pyrite, pyrrhotite and iron oxides in water at 25° C, when total S=10<sup>-6</sup> mol. Log of iron concentration is shown to be -4, the line indicating changes in solubility. The conduction band edge, E<sub>c</sub>, of pyrite is also shown. The potentials relative to the saturated calomel electrode are shown on the right-hand side.

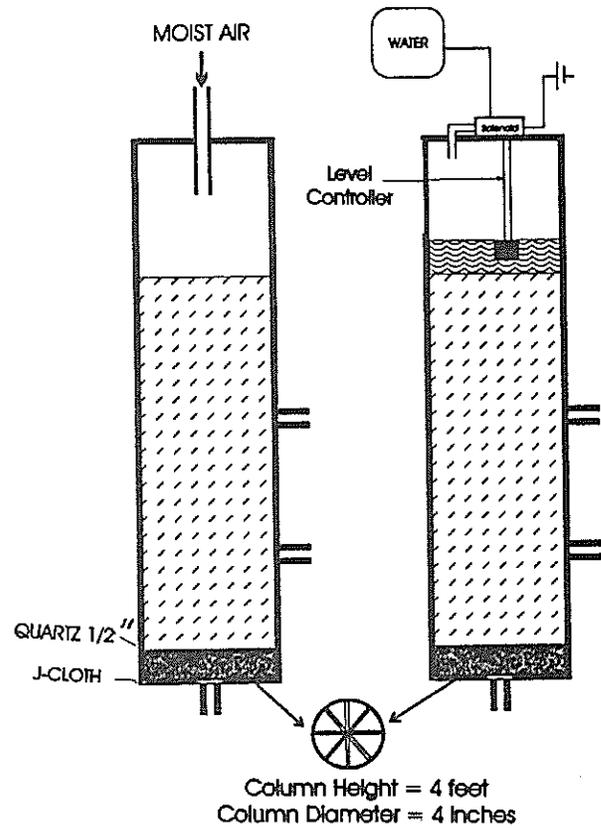


Figure 2. Diagram showing lysimeter design. Lysimeter 2 is provided with a solenoid valve to control water level to 2 in above the tailings.

It follows from the foregoing considerations that it may be possible to control and even prevent the atmospheric oxidation of pyrrhotite and the resultant acid generation by converting the sulfide into an oxide hardpan where each FeS particle is coated with an iron oxide film and the particles cemented together to form a goethite structure.

The following work was therefore undertaken to examine the formation of pyrrhotite hardpans by surface chemical methods and to test their stability and susceptibility to atmospheric oxidation and acid formation.

### Experimental Methods

#### Materials and Equipment

Fresh pyrrhotite tailings in unoxidized form were obtained from the Sudbury (Ontario) area. From image analyses, these tailings were found to contain 78% pyrrhotite, 15% magnetite, 4% silicates, and 3% chalcopyrite, pentlandite, and other minor constituents. The tailings were first oxidized in a slurry form by bubbling air through the slurry for 12 h. These samples are henceforth referred to as "laboratory oxidized" tailings. Another batch of fresh tailings was exposed to air in a steel tray for two weeks in moist condition at room temperature. The tailings were raked frequently for uniform oxidation. These samples are referred to as 'naturally oxidized' tailings in the text to follow.

For large-scale experiments, five cylindrical lysimeters of 4 ft length and 4 in diameter were fabricated from clear plexiglass of 1/8 in wall thickness (fig. 2). A solenoid valve fitted to the top plate of lysimeter 2 and a water reservoir enabled control of the water level automatically to a depth of 2 in above the tailings bed. The following is a detailed description of the procedures. Figures 3 and 4 provide further details of the sample histories and treatment.

**Oxidation and Loading**

The lysimeters were loaded with tailings in slurry form using heavy duty pumps. It took about 48 h for the tailings to settle before the bed could be treated with Fe<sup>2+</sup> solution. The treatment methods are summarized in table 1 in sequential form and are further described below.

Table 1 - Summary of work

Lysimeter	Treatment method					
	Tailings type	Laboratory oxidation	Treatment with Fe <sup>2+</sup>	Curing period 1	pH	Curing period 2
1	Fresh, unoxidized	Yes	Soak and drain method	2 weeks	8.5 on top, 5.5 at bottom	6 to 8 weeks, kept moist
2	Fresh, unoxidized	Yes	Percolation	2 weeks	as in test 1	6 to 8 weeks, kept 2.5 cm solution head
3	Naturally oxidized	No	Soak and drain method	2 weeks	as in test 1	6 to 8 weeks, kept moist
4	As in test 1, without Fe <sup>2+</sup> treatment					
5	Fresh unoxidized	Yes	Intimate mixing	2 weeks	as in test 1	Air

**Treatment with Fe<sup>2+</sup> Solution**

Lysimeters 1, 3, and 4 were treated with a 0.01M solution of Fe<sup>2+</sup> (2.78 g/L of FeSO<sub>4</sub>·7H<sub>2</sub>O) at a pH ~6, by a "soak and drain method" in which the column was first soaked with a solution head and then allowed to drain naturally until the percolant solution contained at least 0.001M of the ferrous salt. In the case of lysimeter 2, the Fe<sup>2+</sup> solution was percolated from the top until the percolated solution at the bottom had acquired the required concentration (~0.001M) of ferrous salt. In the case of lysimeter 5, however, the tailings were intimately premixed with the Fe<sup>2+</sup> solution in the drum itself before being transferred to the lysimeter. Lysimeter 4 was set up for a blank run without any treatment with the ferrous solution.

Tailings in lysimeter 2 were maintained under a constant head of water as described earlier, while column 5 was kept exposed to air under natural, atmospheric conditions.

**Curing Period 1**

After treatment with ferrous salt, the columns were left for an initial period of 2 weeks of curing to allow oxidation of ferrous to ferric iron take place under moist conditions. Extra moisture was maintained in lysimeters 1, 3, and 4 by bubbling air through water aspirators and circulating the moist air on the top of the tailings.

After 2 weeks of curing (period 1), tap water adjusted to a pH of 10.5 was allowed to percolate through the tailings until the percolant solution had reached a pH of at least 6. A pH of 6 was selected because the zero point of charge of iron oxides lies between pH 5.5 and 6.5, at which the solubility of iron oxides is minimum. Also  $\text{Fe}(\text{OH})_3\text{-Fe}_2\text{O}_3$  starts precipitating at about this pH. The tailings were then left for a curing period of 8 to 10 weeks for the hardpan to form.

Since water in lysimeter 2 was kept under constant flowing conditions, the percolant solution in this case was monitored continuously during the 8 week period for pH, Eh, and dissolved iron concentration. The results obtained for all lysimeters at the beginning and at the end of the curing periods are presented in graphical form in figures 3 and 4, respectively.

### Small Scale Experiments

Hardpans were grown by both surface chemical and electrochemical methods using 200 g samples of fresh pyrrhotite tailings in each test. In the former case, samples with and without being surface oxidized were subjected to surface chemical treatment separately in glass tubes of 1 in diameter. The rest of the treatment was the same as in lysimeter 5.

In the second method, the tailings were subjected to cathodic treatment in  $\text{K}_2\text{SO}_4$  solution using a two compartment cell with a frit glass junction. A graphite rod immersed in the tailings bed served as the cathode and an inert metal electrode was used as anode. A potential of -200 to -300 mV (SCE) was applied potentiostatically with a current of  $\sim 0.1$  mA passing through the cell under steady state conditions. Further details may be seen elsewhere (Ahmed, 1991).

## Results and Discussion

### Small Scale Experiments

The electrochemically treated tailings (no  $\text{Fe}^{2+}$  added) and tailings treated with  $\text{Fe}^{2+}$  after oxidation with air hardened in about 6 weeks. The glass walls broke at this stage, most probably due to cementing of the iron oxide in the hardpan with the glass walls and subsequent contraction. No such breakage of walls occurred in plexiglass but shrinkage from the walls was observed. Fresh tailings treated with  $\text{Fe}^{2+}$ , without any surface oxidation, took longer to harden.

The hardpans from these experiments were examined by scanning electron microscopy. The backscattered electron image (BEI) and hardpan photographs are shown in figures 5 to 8. It is seen in figures 6, 7, and 8 that the  $\text{FeS-FeS}_2$  grains in these hardpans are cemented in a goethite (+ lepidocrocite) structure and that the synthetic and natural hardpans of pyrrhotite have the same structure (figs. 7,8). The pyrite hardpan (fig. 6), however, is seen to be separated from the goethite phase by a third phase which seems to be a dehydrated form of iron oxide.

### Lysimeter Tests

Probe tests with nails after the second curing period indicated that the hardening of tailings was confined mainly to the outer layer of the beds exposed to air; the inner core, which was not exposed to air (oxygen), remained soft and retained most of the  $\text{Fe}^{2+}$  in the unoxidized form. Obviously, the  $\text{Fe}^{2+}$  in the inner core of the tailings was not oxidized and not precipitated as ferric oxyhydrate. As a result, the excess of  $\text{Fe}^{2+}$  ( $\sim 0.001\text{M}$ ) drained out through columns 1, 3, 4, and 5 during percolation tests, as shown in fig. 4. The pH of the percolant solutions was between 5 and 6.

**HISTORY**

April 2 Tailings loaded  
 April 6 Initial settling  
 April 8 Solution clearing  
 Fe<sup>2+</sup> Addition started  
 April 29 Fe<sup>2+</sup> Addition ended  
 May 4 pH adjusted; pH<sub>i</sub> = 10.45  
 May 29 Fe<sup>2+</sup> = added to lysmtr. #3

**Redox Potentials**

Fe<sup>2+</sup> Soln. = 0.243 V  
 #5 = 0.046 V (SCE)  
 #2 = 0.120 V (SCE)  
 #1 = 0.186 V (SCE)

**Flow Rates:**  
 0.7 to 0.8 mL /mm

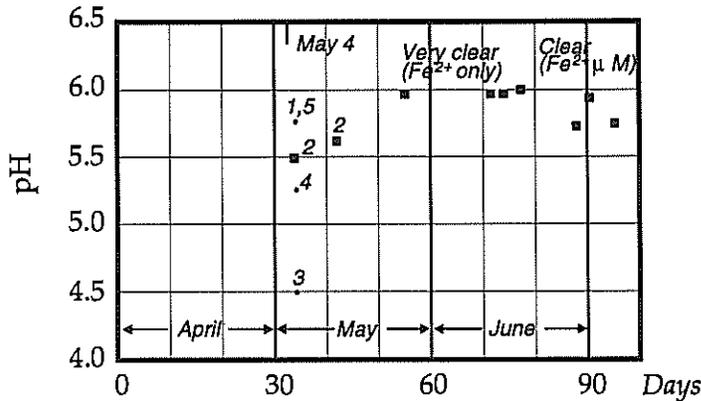


Figure 3. Diagram showing the history and a record of redox potentials, pH and Fe<sup>2+</sup> concentration in the percolating solution, during the first 3 months. The numbers refer to different lysimeters and ● ■ refer to readings for respective lysimeters.

**HISTORY**

Aug 28, 1993  
 Lysimeter 1,2,3,4 and 5 filled with water  
 & percolation tests carried out.

**Redox Potentials :-**

# 1 0.0640 V (SCE)  
 # 2 -0.0230 V (SCE)  
 # 3 0.0834 V (SCE)  
 # 4 0.0653 V (SCE)  
 # 4X 0.1236 V (SCE)  
 # 5 0.0692 V (SCE)

**FLOW RATES**

#2 Uniform 1.07 mL /min  
 #1 Fast 27 mL /min  
 Slow 0.18 mL /min  
 #3 Slow 0.26 mL /min  
 #5 Fast 33 mL /min  
 Slow 0.6 mL /min

Fast and slow refer to flow rates through the annular space (between column and lysimeter wall) and through the tailings column, respectively.

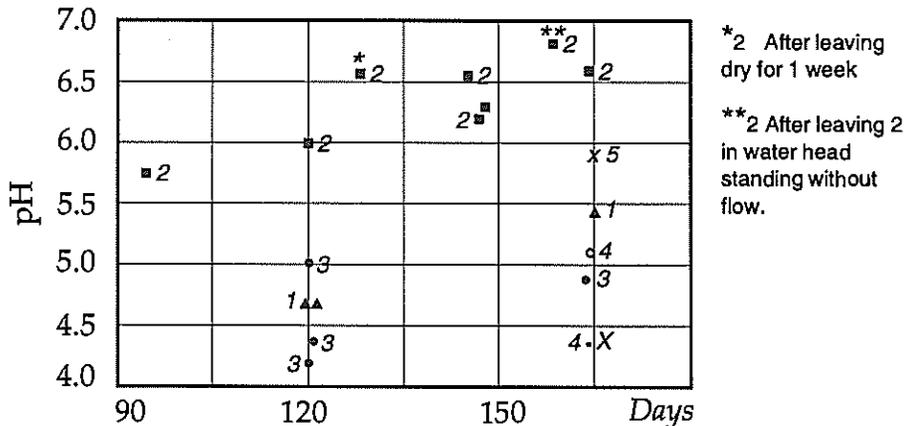


Figure 4. Diagram showing the history and a record of redox potentials, pH and Fe<sup>2+</sup> concentration in the percolating solution, during the last 3 months. The numbers refer to different lysimeters ● ■ refer to readings for respective lysimeters.



Figure 5A. Surface chemically formed pyrrhotite hardpan, obtained after a preoxidation step (pieces shown);

Figure 5B. Surface chemically formed pyrrhotite hardpan obtained without any pre-oxidation.

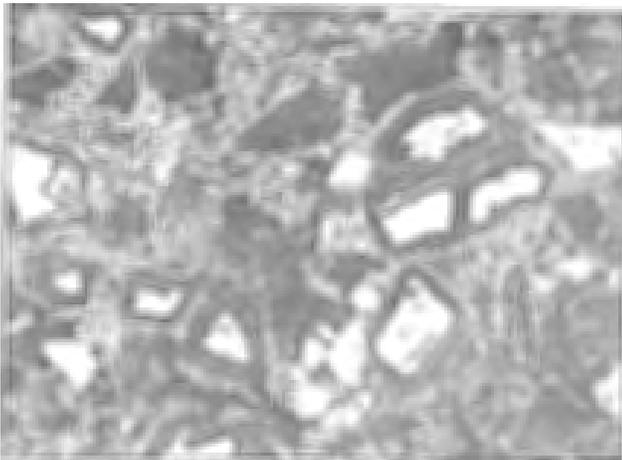


Figure 6. BEI photographs of natural, pyrite hardpan showing FeS<sub>2</sub> grains (white) coated with an iron oxide film, embedded in goethite matrix.

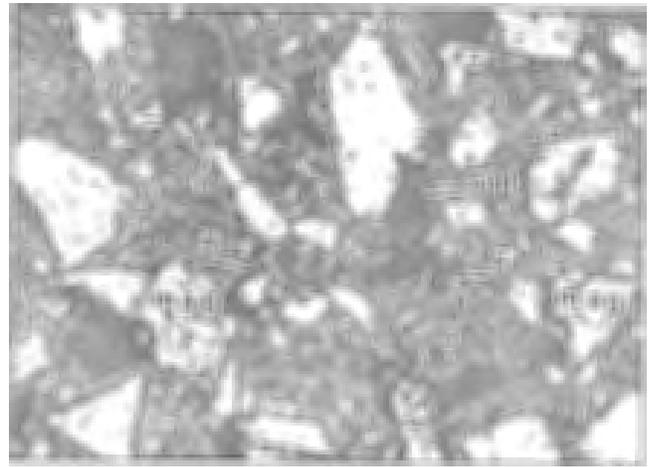


Figure 7. Synthetic hardpan showing pyrrhotite grains embedded in goethite matrix (+ some magnetite). White grains -- FeS.

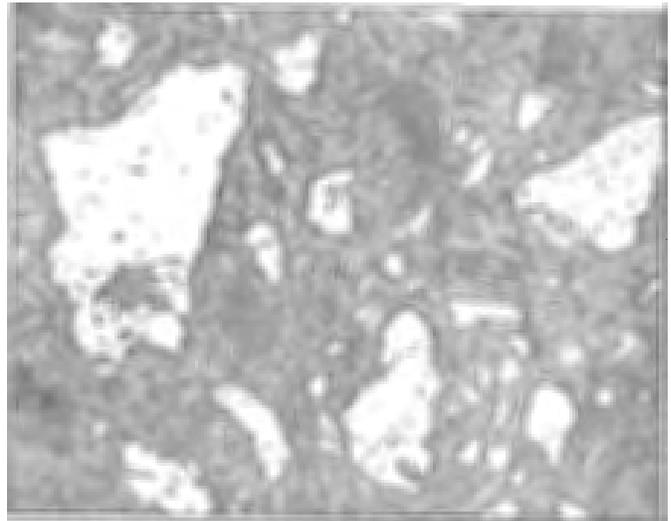
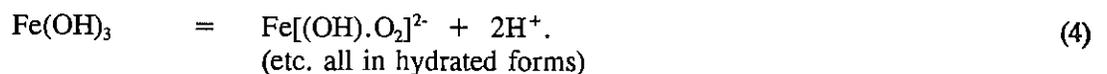
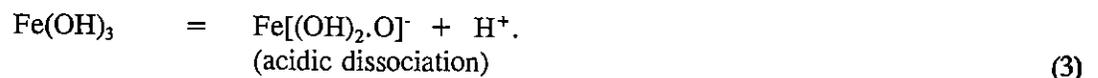
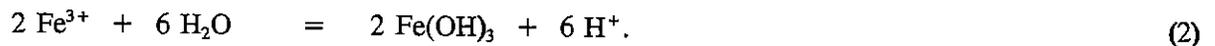
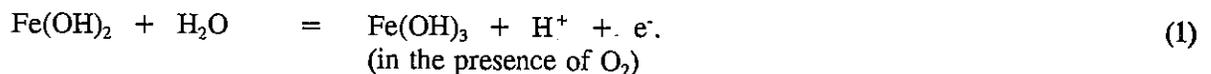
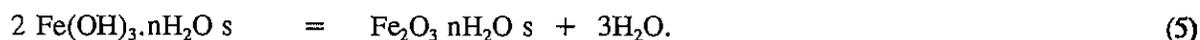


Figure 8. BEI photographs of natural, pyrrhotite hardpan showing FeS grains embedded in goethite matrix.

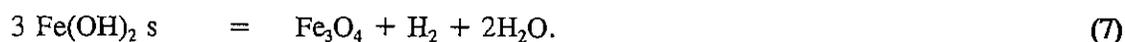
Although the presence of Fe<sup>2+</sup> prevents the air oxidation of the tailings in the inner core, the Fe<sup>2+</sup> in the leachate will eventually add to the acidity owing to hydrolysis reactions as shown below.



The standard free energies of formation (Garrels and Christ, 1965) of the hydrated iron oxides from  $\text{Fe}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  are fairly negative (equations 5-8). Hence, these hydroxides are unstable and should decompose to hematite (goethite) and magnetite as found in the hardpan.



$$\Delta F^0 (\text{Fe}_2\text{O}_3) = - 15.17 \text{ kCal for reaction 5.} \quad (6)$$



$$\Delta F^0 (\text{Fe}_3\text{O}_4) = - 11.1 \text{ kCal for reaction 7.} \quad (8)$$

However, this decomposition will be slow because the activities of the reactants and products (solids) are unity. The hardpan formation is therefore time dependent, but the kinetics can be significantly accelerated by modifying the techniques of surface chemical treatment. The access of oxygen to sulfide tailings for surface oxidation is also kinetically controlled. Both these factors need to be considered in improving the kinetics of hardpan formation.

The  $\text{Fe}^{2+}$  concentration to be used needs to be optimized so that it does not contribute to the acidity significantly. Alternatively, the ferrous iron used should be completely oxidized and precipitated on the sulfides as oxyhydrates before loading the lysimeters. The latter procedure in particular will increase the kinetics of hardpan formation to a great extent.

#### Hardening Effect

The hardening was most pronounced in tailings that were preoxidized in the laboratory, treated with  $\text{Fe}^{2+}$ , and exposed to air with normal humidity (~50%). Except in lysimeter 2 (with a water head), tailings in all lysimeters had hardened from the top and sides to varying degrees, depending on the availability of oxygen in the bed. The most hardened column was 5, where the laboratory-oxidized tailings were intimately mixed with  $\text{Fe}^{2+}$  solution and exposed to air under atmospheric conditions. Tailings exposed to extra moist conditions (lysimeter 1, 3 and 4) by passing air saturated with water vapors, appeared to be less hardened; the least hardened column was 4 which was not treated or very little treated with ferrous iron. Hardening and self-compaction appeared to proceed simultaneously. As a result, the beds had developed cracks and detached from the walls at several places with water droplets condensing in the intermediate space. Water was condensing even in lysimeter 5 which was exposed to air under atmospheric conditions. Hence the condensed water was most probably originating from a dehydration process during hardening of the tailings.

#### E-redox, pH and $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$ Concentration in the Percolant Solutions

The water percolation rates, pH, E-redox and concentration of dissolved  $\text{Fe}^{2+}$ - $\text{Fe}^{3+}$  in the percolating solutions were measured at the beginning of the curing period 1 and at the end of the curing period 2 and the results are shown in graphical form in (figures 3 and 4), respectively. Before taking the end readings, (fig. 4), the trapped air was removed from the lysimeters (except #2) by slowly filling the units from the bottom with tap water having pH 6.5 to 7. The water was then allowed to percolate through the column.

In the case of lysimeter 2 with continuous waterflow, the flow rate, pH and ferrous-ferric concentration in the percolant solution were monitored for the entire period. These results are also shown in figures 3 and 4 for the beginning and the end periods of this work, respectively.

Because of the free space created between the tailing bed and the lysimeter wall, almost all of the water in percolation tests flowed through the column through this space readily in a short period of time (~400 mL in 10

to 15 min). The rest of the water percolated very slowly, most probably through the centre core which was not hardened and remained soft. These two rates are referred to as fast and slow flow rates in fig. 4.

At the starting stage prior to curing period 1 (fig. 3), the pH of the percolant solutions was between 5 and 6 for all columns except that lysimeter 3, with naturally oxidized tailings, had a pH of 4.5. This is because the tailings for this lysimeter were oxidized by exposing to open air in moist condition when much acid must have been produced. This acid was not washed out before lysimeter 3 was loaded and hence accounts for the low pH recorded. The iron content of the percolant solutions in all these runs was also high (0.01 to 0.001M) because the columns were freshly treated with  $\text{Fe}^{2+}$  solutions.

The pH values of the percolant solutions recorded at the final stage of the work and the redox potentials are given in fig. 4. These pH values range from 5 to 5.5 for lysimeters 1, 3, and 4, while column 5 shows a pH of 5.94 and the pH for column 2 (with a constant water head) continue to be well above 6. The lowest pH recorded was 4.92 for column 3, as before. Except for lysimeter 2, the dissolved iron concentration (almost entirely as  $\text{Fe}^{2+}$ ) was rather high, in the range of 0.01 to 0.005M. As discussed earlier, this high concentration of iron in the leachate is originating from the inner core of the tailings as the adsorbed  $\text{Fe}^{2+}$  in this region is not oxidized and precipitated as  $\text{Fe}(\text{OH})_3\text{-Fe}_2\text{O}_3$  owing to insufficient oxygen supply.

#### Behavior of Tailings in Lysimeter 2, under 2 in of Water

The pH of the percolant solution from tailings under 2 in of water was initially 5.5 and became clear in about 6 days, the  $\text{Fe}^{2+}$  concentration being in the m mole range. The pH in later stages was between 5.5 and 6.0, and the  $\text{Fe}^{2+}$  concentration kept decreasing steadily to  $\mu$  mole range (fig. 3). In the final stages of work, as shown in fig. 4, the pH was 6.6; E-redox was -0.023 V(SCE), which is highly reducing; and  $\text{Fe}^{2+}$  concentration was  $10^{-8}$  M with no sign of  $\text{Fe}^{3+}$  present in the percolant solution. The percolant was practically pure water, once excess of  $\text{Fe}^{2+}$  (added initially) was removed. Although the bed had compacted well during the curing period, there was no sign of hardening or hardpan formation.

In one experiment, the pyrrhotite column in lysimeter 2, at the final stage of work, was left filled with water without draining it for a week, followed by draining the water and measurement of pH and dissolved iron concentration. In another experiment, the tailings in column 2 were left dry without any water head for a week, and water was then allowed to percolate through. In both these experiments, the pH of the percolant solution was still close to neutral while  $\text{Fe}^{2+}$  concentration continued to stay low ( $10^{-8}$  M). The untreated tailings under the same conditions would produce both acid and  $\text{Fe}^{2+}$ .

#### Redox Potentials

Redox potentials of 0.046, 0.120, and 0.186 V(SCE) were measured in solutions percolating from lysimeter 5, 2 and 1, respectively, at the beginning (fig. 3). These potentials, although fairly positive in relation to the standard hydrogen electrode, are still in the cathodic range in regard to charge transfer reactions with pyrite and pyrrhotite (Ahmed, 1990,1991). As a result, in this potential range,  $\text{Fe}^{2+}$  can still donate electrons and provide cathodic protection to the sulfide from the atmospheric oxidation.

The redox potentials shown in fig. 4 were measured in the percolant solutions at the final stage, after curing period 2. In general these potentials (fig. 4) are more negative than those at the beginning (fig. 3) and indicate reducing or cathodic conditions available at the  $\text{FeS}$ -solution interface with respect to  $\text{Fe}^{2+}\text{-Fe}^{3+}$  couple. There was experimental evidence to show that the redox potentials inside the bed were more negative than those measured outside, in the presence of air. Under these conditions, oxidation of sulfides by oxygen and  $\text{Fe}^{3+}$  by electrochemical mechanisms is not possible, although oxygen may still chemically attack pyrrhotite if it is not passivated and protected by iron oxide films.

## Stability of Hardened Tailings

The hardened part of the tailings appeared to have good physical stability to withstand water percolation upto a pH of 4.5. In addition to the fully oxidized (type O) forms of the FeS hardpan which are porous and brownish in color, a gray type of unoxidized (type R) FeS hardpan was also encountered in the present work. The type R can be obtained by treating fresh and unoxidized FeS tailings with  $\text{Fe}^{2+}$  and exposing to air under moist or slightly wet conditions. After a few weeks, a hard and a very dense compact pan is formed which is gray in color and resistant to oxidation in dry or moist air because of the presence of  $\text{Fe}^{2+}$  in solid state. However, on immersion in water, surface reactions take place, leading to dissolution and precipitation of brown oxyhydrate of iron as a loose precipitate. The hardpans found in nature are usually a mixture of type O and type R hardpans. These hardpans can be completely stabilized by converting the iron oxide surface into less soluble compounds (solubility  $< \mu\text{M}$ ) of iron such as silicates and carbonates, as suggested by phase diagrams (Garrels and Christ 1965).

## Summary and Conclusions

1. Pyrrhotite hardpans can be prepared on a small scale by surface chemical treatment of the FeS tailings with  $\text{Fe}^{2+}$  under controlled conditions of pH, moisture, and oxygen supply. Such hardpans could also be made by cathodic treatment of the FeS tailings followed by exposure to air. The synthetic and natural hardpans were found to have the same structure, consisting of the FeS grains cemented in a ferric oxyhydrate matrix (goethite + lepidocrocite). The hardpan is formed as a result of the the oxidation of the adsorbed  $\text{Fe}^{2+}$  to the ferric state on FeS surfaces and precipitation of the oxyhydrates in the intergranular spaces. The ferric oxyhydrates then seem to consolidate into a hardpan on aging. Natural hardpans of pyrite are rare in occurrence and have slightly different structure at the pyrite-goethite interface.

2. In large scale experiments using lysimeters, formation of hardpans by surface chemical methods was restricted only to the outer layers well exposed to air. The inner core of tailings which was devoid of oxygen, remained soft and retained  $\text{Fe}^{2+}$  in the unoxidized form. The presence of ferrous iron provides cathodic protection to FeS from air oxidation. During water percolation, however, the excess  $\text{Fe}^{2+}$  ions drain out and contribute to the acidity of the percolant solution. Hence, the  $\text{Fe}^{2+}$  concentration to be used, the pH conditions and aeration methods need to be optimized in the hardpan formation.

3. The formation of hardpan is time dependent and is a slow process due to various factors such as low concentration of the dissolved oxygen in water and its slow diffusion to FeS, if immersed in water. Hence, the oxidation rates of FeS are known to be greatly enhanced in moist conditions where the oxygen has to diffuse through only a few molecular layers of water on the surface compared to tailings in wet conditions under several inches of water. The galvanic cells could be formed on FeS surfaces even in moist conditions. Formation of  $\text{Fe}(\text{OH})_3\text{-Fe}_2\text{O}_3$  is also kinetically slow (eqns. 5-8), as discussed earlier.

Fast methods of forming FeS hardpans can be developed by improving the reaction kinetics of the processes involved. In addition, the  $\text{FeS-Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$  hardpans can be further stabilized by converting the iron oxide surfaces into less soluble compounds of iron such as silicates, by surface chemical methods. This would greatly reduce the equilibrium concentration of the dissolved iron and hence the acidity in the percolant solutions.

4. Whereas the oxidation of pyrrhotite by oxygen is predominantly chemical, the oxidation of pyrite is mainly electrocatalytic in nature. Hence, formation of iron oxide films on pyrite is difficult without changing the surface composition significantly. The present, surface chemical methods therefore were not applicable to pyrite for hardpan formation.

5. The presence of an iron oxide layer on the FeS surfaces would substantially reduce the cross section of the sulfide exposed to oxygen attack. The use of  $\text{Fe}^{2+}$  would further reduce the oxygen flux by reacting with it and eventually forming the ferric oxyhydrate in the inter granular space.

6. The oxidative decomposition of the FeS and of the acid generation can be completely prevented by maintaining about 2 in of water head on the top of the tailings. This effect is not merely due to the lowering of the oxygen flux at the surface and its slow diffusion kinetics as discussed above, but also due to the formation of Fe<sup>2+</sup> ions formed from FeS oxidation. The Fe<sup>2+</sup> provides cathodic conditions to the surface in addition to reacting with oxygen directly as discussed above. Hence treating the tailings with a dilute solution of Fe<sup>2+</sup> further helps in the protection of FeS from oxidation. However, the concentration of Fe<sup>2+</sup> to be used needs to be optimized so that it does not contribute to the acidity of the percolant solution significantly.

In field conditions, the existing beds could be treated with the minimum amount of Fe<sup>2+</sup> to prevent air oxidation and the bed could then be topped with a hardpan formed as above. The iron oxide in the hardpan need to be further stabilized by converting the surface into less soluble compounds of iron so as to completely prevent the dissolution of iron. For new tailings, the entire bed could be converted into a hardpan by applying a fast method of hardpan formation by treating with Fe<sup>3+</sup> in low concentration, followed by hydrolysis. Certain optimization studies need to be conducted in this respect before a large scale method could be developed.

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